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# Approaches for improving the performance of filament-type resistive switching memory

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Resistive random access memory (RRAM) has received significant research interest because of its promising potential in terms of down-scaling, high density, high speed and low power. However, its endurance, retention and uniformity are still imperfect. In this article, the physical mechanisms of filament-type RRAM and the approaches for improving the switching performance, including doping, process optimization and interface engineering, are introduced.

**non-volatile memory, resistive random access memory (RRAM), conductive filament (CF)**

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Many metal-oxide-metal systems show electrically induced resistive switching (RS) effects and have therefore been proposed as the basis for future non-volatile memories [1,2]. Resistive random access memory (RRAM) will also play an important role in the developing field of logic circuits, field programmable gate arrays and memristors [3]. Depending on where RS occurs, various proposed RS models can simply be classified in to two categories: the interface-type, which can be attributed to the modification of the interface barrier height; and the filament-type, which is cell size independent and only occurs in a localized active area. The filament-type RRAM is thought to be suitable for down-scaling to 20 nm and below [2]. However, the intrinsic mechanisms are still divergent and robust cycling endurance, data-retention and performance uniformity must be addressed for commercial applications. The key to improving filament-type RRAM is to effectively control and optimize the concentration and profile of inner mobile ions in the binary transition-metal-oxide (TMO) films. This article introduces the approaches for improving the RS performances of filament-type RRAM, including material modifications and interface engineering.

## 1 Mechanism of the filament-type RRAM

In the filament-type RRAM, RS behavior is dominated by the formation and rupture of local conductive paths inside binary TMO films. R. Waser has proposed two models to expound the origins of a filamentary conductive bridge [1].

One model is based on cation migration (electrochemical metallization memory, ECM) [1]. Under applied voltage, the mobile cations coming from the reactive electrode drift and discharge at the counter electrode, leading to the growth of a conductive filament, and finally the cell is turned to the ON-state. With reverse voltage, an electrochemical dissolution of the conductive bridges takes place, resetting the cell into the OFF-state. The validity of the ECM model was convincingly demonstrated by Yang et al. [4].

Another model is based on anion migration (valence

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change memory, VCM) [1]. Usually, the transition metal in the binary TMO has several valences. For example, $Ti^{4+}$ and $Ti^{3+}$ (equivalent to an oxygen vacancy) ions coexist in the $TiO_2$ lattice, which indicates local nonstoichiometric $Ti_nO_{2n-1}$ (the so-called Magnéli phase) exhibited in the $TiO_2$ film. Under applied voltage, the Magnéli phase filament is extended from anode to cathode because of the generation and movement of oxygen vacancies under a high electric field. When the Magnéli phase filament connects both electrodes, the device transits from the OFF-state to the ON-state attributed to the high conductance of the Magnéli phase. With reverse voltage, the reverse reaction leads to the rupture of filaments, and the device is switched back to the OFF-state. Kwon et al. recently reported the TEM image of the CF in a Pt/$TiO_2$/Pt device [5]. The results of electron diffraction provide strong evidence for VCM theory.

## 2 Performance improvement approaches to filament-type RRAM

The filament-type RRAM has demonstrated high switching speeds (of the order of GHz), large $R_{On}/R_{Off}$ ratio (>$10^7$), low operation voltages (<1 V) and low switching currents (of the order of nanoamperes) [4,8,26]. However, its endurance, retention and uniformity performances have been facing great challenges [1,2]. Many studies have found possible methods for promoting filament-type RRAM [9,18,23]. Whatever methods are used, the key is to control and optimize the concentration and profile of inner mobile ions in the binary TMO films. Generally, the improvement methods can be categorized as the following two types: (1) those that modify the functional materials; and (2) those that optimize the interface between the electrode and functional layer.

### 2.1 Modification of the functional materials

The functional layer materials can be modified in the following two ways: (1) doping the oxide materials; and (2) process adjustment in the fabrication of the oxide film.

(i) Doping the functional layer materials. Doping is an effective way to modify the concentration and distribution of impurities, and is widely used in the semiconductor industry. In the field of RRAM, doping impurities is also an important means to improve the performance of the device. Our group has carried out many studies based on $ZrO_2$ to investigate the effect of doping on the improvement of the performance of the device (as Table 1 shows). Some conclusions can be reached: (1) the initial high electroforming voltage can be eliminated [6–10]; (2) the yield of the devices can be significantly enhanced [8–10]; and (3) the doped devices exhibit more concentrated switching voltage than undoped ones [8–10]. These advantages were also observed in Cu-doped $SiO_2$ [11] and Al-doped ZnO devices [12].

The intentionally introduced impurities are beneficial for providing sufficient mobile ions in the system. It is well known that the electroforming process is similar to the dielectric soft-breakdown process, in which some defects (such as ions or vacancies) are generated [13]. These defects propagate under a high electrical field and form a local conductive filament between the electrodes. As shown in [6–10], the electroforming processes are all removed, indicating enough defects are generated in $ZrO_2$ film after doping. Because of more uniform and homogeneous defects, high device yields (nearly 100%) of doped devices can be achieved [8]. Moreover, more stable RS behaviors occur after doping because the impurities introduced play the role of seeds inside the oxide film [10], providing well distributed anchors for the development of filamentary tracks. Thus the RS characteristics of doped devices are more concentrated.

By analyzing the RS characteristics after doping, we can divide dopants into two basic categories. In ECM-based RRAM, doping Cu, Ag, etc. impurity can increase the concentration of mobile cations [6–9]. While in VCM-based RRAM, more oxygen vacancies will be introduced after doping Ti, Li, etc, because these impurities have a much stronger ability to absorb oxygen [10,14,15]. Based on this characteristic, the Fuji Company reported a Ti-doped NiO RRAM and demonstrated that Ti impurities could produce more oxygen vacancies by SIMS and XPS [14]. However, simply increasing the oxygen vacancies content is not fully effective. How to effectively control the distribution of oxygen vacancy filaments is a key issue to finally improving the RS uniformity. B. Gao et al. indicated doping trivalent elements such as Al, La or Ga into the tetravalent metal oxides such as $HfO_2$ or $ZrO_2$ would lower the forming energy of oxygen vacancies (shown in Table 2), which effectively controls the formation of oxygen vacancy filaments along the doping sites [16].

(ii) Process adjustment during oxide fabrication. As for

**Table 1** Some recently reported results of doping $ZrO_2$ film for characteristics improvement

| Device structure | Yield (%) | Forming process | $V_{set}$ (V) | $V_{reset}$ (V) | On/off ratio | Retention (s) | Switching polarity |
|---|---|---|---|---|---|---|---|
| Au/Cr/$ZrO_2$/$n^+$Si | ~50% | yes | –2.0–3.5 | 1.5–3 | ~$10^3$ | – | – |
| Au/Cr/$ZrO_2$:$Zr^+$/$n^+$Si [6] | ~90% | no | 3.2 | –3.2 | ~$10^6$ | 2500 | bipolar |
| Au/Cr/$ZrO_2$:Au/$n^+$Si [7] | ~90% | no | 4.5–10 | 1.5–4 | >$10^4$ | >$10^6$ | unipolar |
| Cu/$ZrO_2$/Pt | <40% | yes | 0.5–10 | –0.5–1.5 | >$10^4$ | – | bipolar |
| Cu/$ZrO_2$:Cu/Pt [8] | ~100% | no | 2.1–3.6 | 0.8–1.5 | ~$10^6$ | >$10^4$ | nonpolar |
| Cu/$ZrO_2$:Au/Pt [9] | ~100% | no | 2–5 | 0.5–1.2 | >$10^4$ | >$10^6$ | nonpolar |
| Cu/$ZrO_2$:Ti/Pt [10] | ~100% | no | 1–4 | –0.5–1.5 | >$10^4$ | >$10^7$ | bipolar |

**Table 2** Summary of the forming voltage of oxygen vacancy[a)]

| | Undoped (eV) | Ti-doped (eV) | Al-doped (eV) | La-doped (eV) | Ga-doped (eV) |
|---|---|---|---|---|---|
| $HfO_2$ | 6.53 | 6.48 | 4.09 | 3.42 | – |
| $ZrO_2$ | 6.37 | 6.11 | 3.66 | 3.74 | 3.77 |

a) Data comes from [16].

VCM-based RRAM, the oxygen content and distribution is closely related to the process recipe of the oxide film deposition, such as the oxygen content in the preparation, the film deposition rate and the post-annealing temperature, etc. [17–19].

Different oxygen content (defined as $P(\%) = P(O_2)/P(O_2+Ar)$, P stands for percentage) in the sputtering atmosphere affects the characteristics of oxide films. When the oxygen content increased from 5% to 10%, the resistance value of the NiO film drastically increased, but when the oxygen content increased to 20%, the RS behavior disappeared [17]. This phenomenon demonstrates a moderate amount of Ni vacancies and corresponding cavities can improve switching behavior.

Annealing processes after fabricating the film can improve the film crystallinity, providing more grain boundaries, thus the conductive filament can easily be formed. For some VCM-type RRAM containing oxidizable metal (for example Ti), annealing has great influence on the concentration of oxygen vacancies. As the annealing temperature increases, the oxygen content in the oxide film decreases because of oxygen diffusion and absorption of the oxidizable metal, thus stronger conducting paths with a higher density of oxygen vacancies are created between the two electrodes, leading to the decrease in the forming voltage [19].

## 2.2 Interface engineering

Another important method for controlling the concentration and profile of mobile ions is interface engineering, which mainly includes: (i) selecting a proper electrode; and (ii) inserting a buffer layer between the electrode and oxide film.

(i) Changing the electrode to optimize the interface. The basic memory cell of ECM-based RRAM is a two-terminal element consisting of a solid electrolyte layer sandwiched between an inert and a reactive electrode. The top and bottom electrodes are generally specified, with Ag or Cu as the reactive electrode and Pt, W or IrO as the inert electrode [2].

For VCM-based RRAM, different electrodes will cause different behaviors on the interface and device performance. A group of TEM images of the interface engineering are shown in Figure 1. These changed interfaces are composed of oxides of the metal electrode. The reason for the oxidation of the metal electrode is that it has less Gibbs free energy ($\Delta G_0$) than the metal element in the oxide film. Less $\Delta G_0$ means a higher capability to combine with oxygen

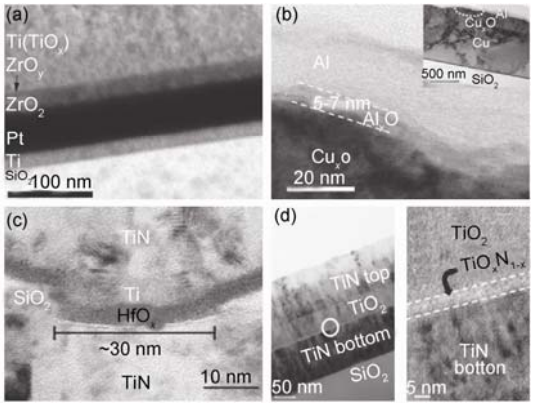


**Figure 1** (a) HRTEM image of a thin $ZrO_y$ interface layer formed between Ti ($TiO_x$) and $ZrO_2$ [21]. (b) Cross-sectional TEM image of the Al/$Cu_xO$/Cu structure. A clear 5–7-nm-thick interface layer was observed between Al and $Cu_xO$ [23]. (c) XTEM image of TiN/$TiO_x$/$HfO_x$/TiN device with concave structure [25]. (d) TEM image of TiN/$TiO_2$/TiN cell [24].

[20]. Using such an electrode can produce more oxygen vacancies by absorbing the oxygen in the film, which can make the filament form easily. As shown in Figure 1(a) [21], Ti absorbs oxygen from $ZrO_2$ film, forming $TiO_x$ and $ZrO_y$ on the interface, which makes the oxygen focus in a localized area, thus the conductive filament formation and disruption is localized. Lin et al. have investigated the influence of different types of electrode materials on the interface between the switching layer and the electrode [22]. Commonly, when oxygen-rich oxide materials are used as the switching layer, utilizing TiN, Ti or Li as TE, which can generate plenty of oxygen vacancies, will greatly improve the RS performance.

In summary, the ECM-type RRAM needs specified electrodes, while for VCM-based RRAM, Ti or TiN electrodes as oxygen reservoirs can provide sufficient nonlattice oxygen ions to recover the oxygen vacancies and form filaments, which will optimize the interface and therefore maintain good switching endurance and retention in the RRAM devices.

(ii) Using a buffer layer to optimize the interface. Introducing a thin buffer layer between the electrode and the functional layer is another effective way to optimize the interface.

As for VCM-based RRAM, the material of the buffer layer is usually oxidizable metal or metal oxide, such as Ti or $TiO_2$, which is as thin as several nanometers [24–26]. The reason for using such a buffer layer is as follows: for this type of RRAM, the filament formation and rupture are associated with the distribution of movable oxygen ions and oxygen vacancies in the oxide films, and such an oxidizable buffer layer can be considered as the oxygen reservoir to help stabilize the local oxygen migration for the filament formation and rupture (the role is similar to that of the reactive metal electrode discussed previously). According to the RS mechanism of filament-type RRAM discussed above,

the RS characteristics will be more stable and reliable if the regions where the formation and rupture of the filaments occur can be controlled. By using a thin Ti layer as the reactive buffer layer between the anode and $HfO_2$, excellent memory performances have been demonstrated by Tsai's Group [25]. They also adopted a thin $AlO_x$ buffer layer under the $HfO_x$ to enhance the read disturb immunity of the device [26]. The stacked buffer layer can effectively control the concentration and profile of the mobile oxygen ions, thus leading to a great improvement in the uniform performance of the device.

## 3 Conclusions

The improvement in the performance of RRAM is crucial for practical applications. According to the mechanism of filament-type RRAM, a means of improving the performance of the device should be considered, including ways to control the concentration and profile of inner mobile ions in the functional layer. This article discusses the approach from the following perspectives: modifying the material of the functional layer and optimizing the interface between the electrode and the functional layer. Both doping and process adjustment in fabricating the oxide film can modify the concentration of mobile ions in the functional layer. Changing the electrode or using a buffer layer can achieve the purpose of optimizing the interface between the electrode and the functional layer. Further research is needed to definitively elucidate the 'microscopic' mechanism, which will ultimately provide guidelines for improving RRAM performance.

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